

Monitoring and Quality Control of Diesel Fraction Production Process

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Abstract. In this work the mathematical model of diesel fraction and atmospheric gasoil catalytic dewaxing process has been developed. Also the pattern of applying the created model to solving such problems as monitoring and quality control of diesel fraction production in the catalytic dewaxing process. It has been represented that to meet such challenges, the model should take into consideration thermodynamic and kinetic laws of hydrocarbon conversion on the catalyst surface, and instability factors that are specified by catalyst deactivation. The developed model allows controlling the quality of obtained diesel fraction depending on feed and temperature regime in the reactor. The value of model calculation absolute error does not exceed 2%, which corroborates the adequacy of the model to actual process. The computations using the model have shown that to provide the desired product yield (not less than 40% wt. of overall yield of the unit products) of programmed quality (cold filtering plugging point not higher than minus 34°C for winter diesel fuels and not lower than minus 40°C for arctic ones) at long-time catalyst operation (during 4 years), it is necessary to sustain the reactor temperature at the average level of 19°C higher than when working with fresh catalyst. This must be done to compensate catalyst activity loss due to its deactivation.

1. Introduction

Industrial catalytic processes of petroleum refining sector represent complex chemical technology systems that require qualified control and operation. Optimization of technological process is of a high difficulty level due to its instability presented by continual changing of feed fraction compositions, variations of operating modes, proceeding chemical reactions and catalyst deactivation. Simultaneous introduction of all mentioned factors is impossible in real terms. Consequently, the challenge of forecasting the operation modes of complex commercial units within the instable conditions is multitask and labor intensive.

This challenge is successfully met applying mathematical models, developed in terms of fundamental laws of hydrocarbon conversion on the catalyst surface, considering the instability factors and mutual influence of every of adjacent processes being conducted in a single chemical technology system [1, 2, 3]. Application of these models allows forecasting the behavior of complex chemical technology system at the constantly changing conditions of the process [4, 5].



2. Experimental

The technology of catalytic dewaxing is successfully applied to obtain winter, summer and arctic grades of diesel fuel with improved cold flow properties [6]. This is a complex chemical technology system which involves the interconnected stages of hydrotreating, hydrodewaxing, stabilization and fractionation [1, 2].

During the process a stable naphta, diesel fraction with improved low-temperature properties, and residue with a boiling point of above 340 degrees of Celsius are obtained.

The process proceeds in three reactors in hydrogen environment. The first two reactors are hydrotreating reactors with a nickel-molibdenum catalyst, the third one is a dewaxing reactor with nickel catalyst. Process temperature is 350–400°C. The reactions of hydrocracking, hydroisomerization, hydrogenation of unsaturated hydrocarbons, hydrogenation of mercaptanes followed by hydrogen sulfide formation, aromatization and coke formation take place.

After reactor section the products enters the stabilization column, where the light hydrocarbons, hydrogen sulfide and water are eliminated. The stable hydrogenate subsequently flows to the rectification section, where it is fractionated into products, such as gasoline and diesel fraction.

Based on experimental data from the industrial unit, also with the application of quantum chemistry method, realized within the frames of Gaussian software, thermodynamic reaction parameters have been defined, and formalized reaction network in the dewaxing reactor has been made (Figure 1).

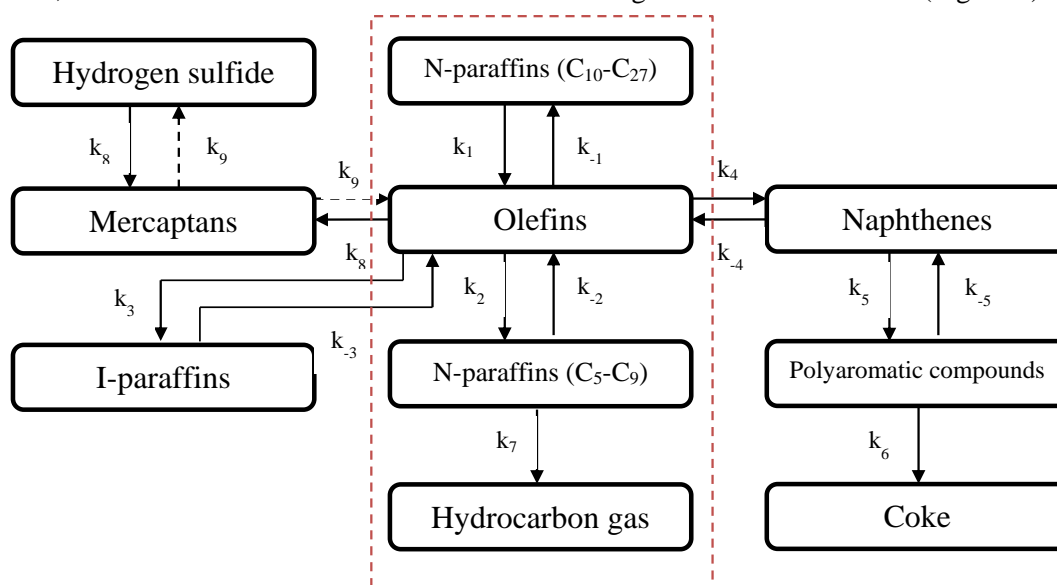


Figure 1. Formalized scheme of catalytic dewaxing reactions.

Primary reactions of the process are the reaction of hydrocracking of high-molecular unbranched alkanes and the reaction of dehydrogenation of low-molecular alkanes with further isomerization, through the stage of olefin formation [7, 8]. The main secondary reaction is coke formation.

According to the formalized reaction scheme the kinetic description of the process has been made. The kinetic model represents the system of differential equations of changing reacting agent concentrations depending on feed residence time.

To maintain the optimal catalyst activity during the middle distillate refining, aimed to obtain the required product volume of specified quality, it is necessary to correct the operating modes of the dewaxing reactor. Thus, to decrease the catalyst deactivation and to sustain optimal activity, the feed is mixed with hydrogen-containing gas (HCG) and the reactor temperature is increased. In this case hydrogen gas reacts with formed polyaromatic hydrocarbons, which may invoke the process of coke formation, hydrogenates these compounds and leads to intensification of olefin and mercaptane hydrogenation.

On the other hand, excess amount of hydrogen may result in intensified hydrocracking reactions followed by reduction of desired diesel fraction yield. Therefore, the main task of controlling the dewaxing catalyst deactivation process is determination of optimal HCG/feed ratio under the conditions of changing flow rate, feed composition and temperature inside the reactor.

To control the dewaxing catalyst deactivation process under the conditions of changing feed composition the deactivation function has been added to the mathematical model of the dewaxing process [9-11]. The mathematical model represents the system of differential equations of mass and heat balance. Mathematical model considering deactivation process is shown below:

$$\begin{cases} G \cdot \frac{\partial C_i}{\partial z} + G \cdot \frac{\partial C_i}{\partial V} = \sum_{j=1}^m a_j \cdot W_j \\ G \cdot \frac{\partial T}{\partial z} + G \cdot \frac{\partial T}{\partial V} = \frac{1}{\rho \cdot C_p^{mix}} \sum_{j=1}^m Q_j \cdot a_j \cdot W_j \end{cases}, \quad (1)$$

Initial conditions: $z = 0$: $C_i = C_{i,0}$; $T = T_0$; $V=0$: $C_i = C_{i,0}$; $T = T_0$, where z is a volume of the refined feed from the moment of fresh catalyst charge, [m^3]; G is the feed flow rate, [m^3/h]; $z = G \cdot t$ (t is a catalyst operating time from the moment of fresh catalyst charge, [h]); C_i is a concentration of i -component, [mole/l]; V is a catalyst bed volume, [m^3]; a_j is a catalyst activity in j -reaction; ρ is a mixture density, [kg/m^3]; C_p^{mix} is a specific heat capacity of the mixture, [$J/(kg \cdot K)$]; Q_j is a heat effect of j -reaction, [$J/mole$]; T is a temperature, [K]; W_j is a j -reaction rate, [mole/(l·s)]; m is a number of the reactions.

This model takes into account catalyst deactivation [12, 13]. Catalyst activity can be determined as a proportion of reaction rate constant at any time to the reaction rate constant at the initial moment of the time when the fresh catalyst had been charged:

$$a_j = \frac{k_{j,t}}{k_{j,0}}, \quad (2)$$

where $k_{j,0}$ is a j -reaction rate constant at the initial moment of time (with the fresh catalyst); $k_{j,t}$ is a j -reaction rate constant at the current moment of time. In should be notices that catalyst activity depends on coke concentration on the catalyst surface, and can be defined as an equation:

$$a_j = A_j \cdot e^{-\alpha_j \cdot C_K}, \quad (3)$$

where A_j , α_j are the deactivation coefficients; C_c is a coke concentration, [% wt].

3. Results and Considerations

Created mathematical model for controlling the quality of diesel fraction production process has been checked for adequacy by comparing the calculated data with experimental data from the industrial unit. The error values of calculation of the main hydrocarbon groups, found in diesel fraction, are presented in Table 1. The error does not exceed 2% which corresponds to the error of chromatographic analysis, usually used to determine hydrocarbon content. The model is suitable for the process and can be applied for identification of the process laws, forecast calculation conduction and optimization, providing resource efficient production by control of unit operation modes, product quality and catalyst deactivation process.

Table 1. Calculated and experimental data comparison.

Product (experimental), [% wt.]	Product (calculation), [% wt.]	Error (absolute), [% wt.]
n-paraffins C ₁₀ –C ₂₇		
10.17	11.18	1.01
13.54	11.85	1.69
10.08	10.19	0.11
9.32	9.48	0.16
i-paraffins		
26.46	26.40	0.06
22.95	24.1	1.15
24.66	24.82	0.16
23.14	25.67	2.53
Olefins		
1.74	1.99	0.25
2.63	2.58	0.05
3.07	2.35	0.72
2.25	2.35	0.10
Polyaromatic compounds		
20.53	20.06	0.47
19.90	20.09	0.19
18.53	19.23	0.70
19.30	19.73	0.43

It is well known that during the catalytic dewaxing process the catalyst deactivation takes place due to the reaction of coke formation and sulfur-poisoned acid and metal catalyst sites [13-14]. Application of developed model, which considers deactivation function, helped to prove the fact that during the period from 2012 to 2016 slight decrease of diesel fraction yield from 90 to 44 [% wt.] has been occurring, and the gasoline fraction yield has been increasing from 8 to 20% at the same time (Table 2).

This shows attenuation of hydrogenation reactions which leads to reduction of diesel fractions yield, and intensification of cracking reactions which leads to enhancement of light fractions yield. It should be noticed that increase of the unconverted residue yield (fraction with a boiling point of more than 340°C) (Figure 2) indicates the reduced catalyst activity and decreased feed conversion.

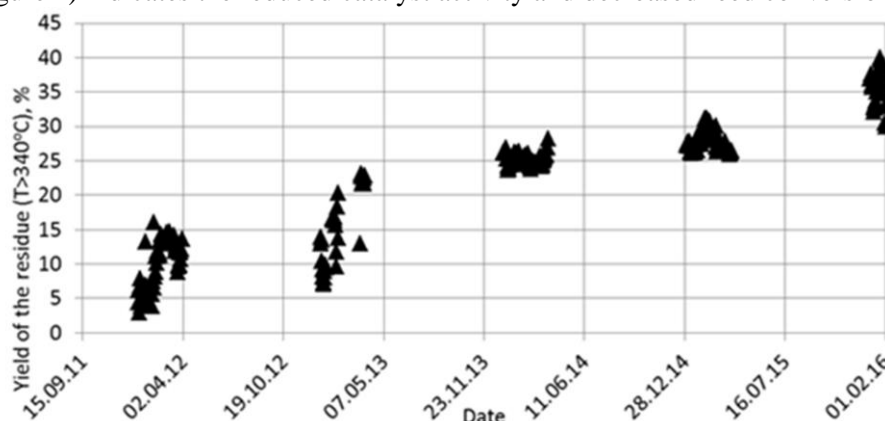


Figure 2. Yield of the residue (T > 340°C) in the dewaxing process during the period of 2012-2016 y.

Table 2. Yield of all fractions in the dewaxing process in the period of 2012-2016.

Year	2012	2013	2014	2015	2016
Yield of diesel fraction, [%]	74 – 90	63 – 88	52 – 65	54 – 60	44 – 52
Yield of gasoline fraction, [%]	8 – 10	10 – 12	15 – 18	18 – 20	20 – 21
Yield of residue fraction >340 [°C]	5 – 15	10 – 25	25 – 30	30 – 35	35 – 40

The computations using the model have shown that to provide the desired product yield (not less than 40 [% wt.] of overall yield of the unit products) of programmed quality (cold filtering plugging point not higher than minus 34°C for winter diesel fuels and not lower than minus 40°C for arctic ones) at long-time catalyst operation (during 4 years), it is necessary to sustain the reactor temperature at the average level of 19°C (Table 3) higher than when working with fresh catalyst. This must be done to compensate catalyst activity loss due to its deactivation, which amounted to 32% by the last year of catalyst operation (2016 y.).

Table 3. Computation of the deactivation compensating temperature.

Date	Yield of fraction 240-340 (DF), [%]	CFPP, [°C]	T _{in} R-3 (actual), [°C]	T _{in} R-3 (comp.), [°C]	ΔT, [°C]
25.01.2016	41,4	-34	341	318	23
27.01.2016	41,8	-37	352	332	20
29.01.2016	41,5	-44	360	345	15
05.02.2016	43,0	-41	369	350	19

4. Summary

To meet the challenges associated with monitoring and quality control of diesel fraction production in the catalytic dewaxing process the mathematical model, developed considering thermodynamic and kinetic laws of hydrocarbon conversion on the catalyst surface, and instability factors that are specified by catalyst deactivation, can be used.

The proposed mathematical model allows defining the optimal operating modes of the reactor block, such as process temperatures and feed flow, and controlling production of the product of programmed quality, which implies hydrocarbon composition and yield of diesel fraction, cold filtering plugging point, and can be used for solving the tasks of increasing resource efficiency of large tonnage industrial catalytic processes.

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